

Application No. 10/827,072

REMARKS

Claims 1-20 are pending, and claims 11-20 are withdrawn as being directed to a non-elected species. Claims 21-33 are canceled without prejudice in view of the restriction requirement.

Applicants note that withdrawn claims 11-20 are maintained. It is respectfully suggested that these materials can be examined together with claim 1-10 without significant additional effort since Ni and Co have similar chemical properties that make them common substitutes for each other in battery materials. Thus, they are commonly discussed together in references. This is true for US 6,638,662B cited in the discussion below.

Rejection Over Kaneda et al.

The Examiner rejected claims 1-3, 5, 7-10 under 35 U.S.C. § 102(e) as being anticipated by U.S. Patent 6,638,662 to Kaneda et al. (Kaneda). The Examiner points to column 6, lines 51-59. However, this text includes a clear typographical error in the critical portion. This issue is explained in the following. In view of the error in the text, Kaneda does not *prima facie* anticipate Applicant's claimed invention. Applicant respectfully request reconsideration of the rejection based on the following.

As noted by the Examiner, Kaneda states at column 6, lines 51-59: "These [composite oxide] materials have an average particle size of preferably 3 to 40 nm." This is the only general reference to the composite oxide cathode material size. But the error is immediately clear from a review of specification generally and in particular the examples. With respect to the examples, see column 10, lines 55-56 ("For the positive electrode-active material, LiCoO₂ powder having an average particle size of 10 μm was used."), column 12, lines 3-5 ("For the positive electrode material, LiNi_{0.8}Co_{0.2}O₂ having an average particle size of 10μm was used."), column 12, lines 40-44 ("A coin-type battery was produced therefrom in the same manner as in Example 1, where

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LiMn₂O₄ having an average particle size of 10 μ m was used as a positive electrode material."), column 15, lines 20-21 ("For the positive electrode material, LiMn₂O₄ having an average particle size of 10 μ m was used."), column 15, lines 59-64 ("LiCoO₂ having an average particle size of 10 μ m as a positive electrode-active [sic] material, scale form graphite having an average particle size of 5 μ m as a positive electrode electroconductive material, PVDF as a binder and 20 μ m-thick Al foil as a positive electrode current collector."), column 17, lines 30-34 ("A mixture of Li_{1.09}Mn_{1.91}O₄ having an average particle size of 10 μ m, scale-formed natural graphite and pvdf in a ratio of 90:6:4 by weight was mixed with N-methylpyrrolidone and thoroughly kneaded to prepare a slurry."), column 23, lines 20-22 ("LiNi_{0.8}Co_{0.2}O₂ having an average particle size of 10 μ m was used for the positive electrode material."), and column 23, lines 62-63 ("For the positive electrode-active material, LiCo_{0.2} [sic LiCoO₂] powder having an average particle size of 10 μ m was used.").

Thus, every example teaches 10 micron average particle size for the lithium metal oxides in the cathode, which is a factor of 250 times larger than 40 nm. The statement of the preferred average particle size was clearly referring to 3-40 microns and not 3-40 nm. This is further confirmed by reference to the Japanese priority document. A machine translation from the JPO web site is attached. On page 5 of the translation, paragraph 0026 corresponds with the paragraph at column 6, lines 51-59 of the Kaneda U.S. patent. At paragraph 0026 of JP 2000-243396A, it is stated (emphasis added) that "These matter has the desirable mean particle diameter of 3-40 micrometers." This confirms what is clearly true from the examples of Kaneda.

Thus, the one vague reference in Kaneda would clearly be interpreted correctly by a person of ordinary skill in the art in view of the specification as a whole as referring to 3-40 microns and not 3-40 nm. This discussion further emphasizes that the reference does not teach

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how to practice Applicant's claimed invention. The reference does not provide a reasonable expectation of success with respect to producing Applicants claimed compositions.

In view of the correction to the typographical error, Kaneda does not render Applicant's invention *prima facie* anticipated. Applicant respectfully requests withdrawal of the rejection of claims 1-3, 5, 7-10 under 35 U.S.C. § 102(e) as being anticipated by Kaneda. While Applicant does not acquiesce with respect to issues relating specifically to the dependent claims, these issues are not specifically discussed since they are moot in view of the issue raised above. In view of these deficiencies, Applicant does not specifically comment further on the issues relating to the dependent claims although Applicant does not acquiesce with respect to these issues.

Rejection of Claims 6 and 7

The Examiner rejected claims 6 and 7 as Kaneda as applied above and further in view of U.S. patent 6,534,216B to Narukawa et al. (Narukawa). However, we believe that the Examiner intended to reject claims 4 and 6 since claim 7 was rejected above as anticipated by Kaneda. Applicant respectfully requests clarification on this issue. The Examiner cites Narukawa for teaching substitutions of various metals for a portion of the cobalt in lithium cobalt oxides. However, Narukawa does not make up for the deficiencies of Kaneda with respect to the claimed invention. Applicant respectfully requests reconsideration of the rejection based on the following comments.

Narukawa does not make up for the deficiencies of Kaneda. In particular, see Fig. 6 of Narukawa. The average particle sizes range from about 7 microns to about 20 microns. The average particle sizes in Narukawa are almost two orders of magnitude larger than Applicant's claimed particle size, which has an upper limit of about 100 nanometers. Thus, the combined teachings of Kaneda and Narukawa do not render Applicant's claimed invention *prima facie* obvious.

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Furthermore, Narukawa does not teach the specific stoichiometries of $\text{Li}_2\text{CoMnO}_4$ or $\text{Li}_2\text{CoAlO}_4$. Therefore, the vague reference to substituting a portion of the Co for another metal does not render the specific compositions in claim 4 and 6 *prima facie* obvious.

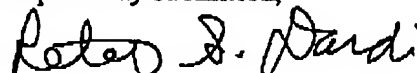
Since the combined teachings of Kaneda and Narukawa do not render Applicant's claimed invention *prima facie* obvious, Applicant respectfully requests withdrawal of the rejection of claims 6 and 7 as Kaneda as applied above and further in view of Narukawa.

CONCLUSIONS

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,



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approach the approach of covering with carbonaceous the element particle which forms alkali metal and an alloy covers particles, such as Mg, aluminum, and Si, by carbonaceous in JP,10-3920,A is proposed as an approach of on the other hand improving the cycle life of the element which forms alkali metal and an alloy. However, as for these carbon covering material, reduction to which a metallic element oxidizes in process of charge and discharge, conductivity falls to, and a charge-and-discharge property falls remarkably is checked.

[0004] The purpose of this invention improves property degradation and is to offer the electrical machinery and apparatus which is high capacity and used it for the high lithium secondary battery and its manufacture approach list of a charge-and-discharge cycle property.

[0005]

[Means for Solving the Problem] Paying attention to the degradation device of the matter which is high capacity as a negative-electrode active material, by controlling the degradation, artificers are high capacity and came to invent the lithium secondary battery of a long cycle life.

[0006] This inventions are a positive electrode, a negative electrode containing the negative-electrode active material which can occlusion emit a lithium ion, and a lithium secondary battery that consists of the nonaqueous electrolyte or polymer electrolyte of lithium ion conductivity, and are characterized by consisting of the oxides and carbonaceous materials containing at least 1 element with which said negative-electrode active material is chosen from Si, Sn, germanium, aluminum, Zn, Bi, and Mg, and laying said oxide under the carbonaceous material. It is desirable that graphite carbon or its floc adjoins said oxide, and said oxide is especially laid under the carbonaceous material as a whole.

[0007] In the lithium secondary battery with which this invention has a positive electrode, a negative electrode containing the negative-electrode active material which can occlusion emit a lithium ion, and the nonaqueous electrolyte or polymer electrolyte of lithium ion conductivity The invasion desorption nature particle which said negative-electrode active material becomes from either [at least] the metal particles which raise the invasion desorption nature of said lithium ion between said positive electrodes and negative electrodes to said carbonaceous material at the time of a carbonaceous-material particle and charge and discharge, or a metallic-oxide particle is included. It has the end of composite powder this invasion desorption nature particle was embedded 50% of the weight or more in said carbonaceous-material particle. 5 micrometers or less, mean particle diameter is desirable and 0.2-2.5 micrometers and having [preferably / 95 % of the weight or more]-90% of the weight or more-particle size of 10 micrometers or less; or an invasion desorption nature particle said invasion desorption nature particle in said carbonaceous-material particle 50 % of the weight or more, Have the end of composite powder it was embedded 80% of the weight or more preferably, and being [this end of composite powder / preferably / 95 % of the weight or more / the particle size of 50 micrometers or less]-90% of the weight or more; or an invasion desorption nature particle has the end of composite powder 50 % of the weight or more was embedded in said graphite particle. 80% of the weight or more, it is desirable, 90 - 95 % of the weight and a rhombohedral crystal are desirable 20 or less % of the weight, and said graphite particle has a hexagonal crystal in 5 - 10% of the weight of the lithium secondary battery which comes out on the other hand at least, and is characterized by a certain thing.

[0008] As for said metal particles or a metallic-oxide particle, it is desirable to consist of at least one metal or oxide of Si, Sn, germanium, aluminum, Zn, Bi, Mg, Pb, Sb, B, In, Ga, Tl, P, As, Pd, and Pt.

[0009] A crystalline substance is 97 % of the weight or more preferably 95% of the weight or more, and a graphite particle can contain 3 or less % of the weight of an amorphous substance preferably 5 or less % of the weight.

[0010] The above-mentioned oxide particle is laid under the carbonaceous material, and spacing of the field (002) of said carbonaceous material by (1) X-ray diffraction method said negative-electrode active material 0.3350nm or more 0.3650nm or less, (2) The peak intensity ratio of 1360cm⁻¹ to 1580cm⁻¹ by argon laser RAMAN of said carbonaceous material 2.0 or less [0.15 or more] (3) -- the mean particle diameter of said oxide -- 10 micrometers or less and (4) -- by including the active material with which are preferably satisfied of two or more at least one or more of the conditions whose specific surface area of said negative-electrode active material is four, 100m² / below g**, more than 1m² / g It can consider.

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as the lithium secondary battery which is excellent in a property.

[0011] In the manufacture approach of a positive electrode, the negative electrode containing the negative-electrode active material which can occlusion emit a lithium ion, and the lithium secondary battery that consists of the nonaqueous electrolyte or polymer electrolyte of lithium ion conductivity Said negative-electrode active material repeats mechanical grinding and a mechanical pressure welding according an above-mentioned oxide particle and an above-mentioned carbonaceous particle to a ball mill. It is manufactured by the approach of mixing a pad, the approach of heat-treating further or the above-mentioned oxide particle, and a carbon precursor, and carrying out carbonization processing of 80% of the weight or more of the oxide particle into a carbonaceous particle, preferably, 50% of the weight or more. Moreover, after laying said oxide particle underground 80% of the weight or more preferably 50% of the weight or more in a carbonaceous-material particle by the approach of repeating mechanical grinding and a mechanical pressure welding according an above-mentioned oxide particle and an above-mentioned carbonaceous particle to a ball mill, or heat-treating further, it is manufactured by the approach of mixing a carbon precursor further and carrying out carbonization processing.

[0012] said oxide -- AB_xO_y (it is chosen out of A:Si, and Sn, germanium, aluminum, Zn, Bi and Mg -- 1 element) At least 1 element preferably chosen from Si, Sn, germanium, Mg, B:Si, and Sn, germanium, aluminum, Zn, Bi, Mg, P, B, calcium, K, Na, Li and F, $x=0-1.5$ -- desirable -- 0-1.0, and $y=1.0-5.5$ -- desirable -- the oxide of a presentation of 1.0-4.0 -- it is -- a crystalline substance -- or [especially] an amorphous substance is desirable. The value of x is the sum of the mole ratios of all the elements chosen as B.

[0013] Moreover, the electric vehicle where mileage is long can be supplied by carrying the group cell which consists of lithium secondary batteries of this invention in an electric vehicle. Moreover, the lithium secondary battery of this invention can be used also not only as an electric vehicle but as a cell for hybrid cars.

[0014] As said oxide SiO , SnO , GeO , $SiSnO_3$, $GeSnO_3$, $SiGe$ 0.5O1.5, SoP 0.2B0.2O2, $GeSi$ 0.1O2.2, GeP 0.5O3.25, $GeBO$ 2.5, $SnSi$ 0.7aluminum0.1B0.1P0.1O2.95, Although $SnSi$ 0.8Mg0.2O2.8 grade is mentioned, what is necessary is just the oxide or multiple oxide which is not necessarily limited to especially these and can carry out insertion desorption of the Li electrochemically within the above-mentioned presentation.

[0015] As for the above-mentioned oxide particle in a negative-electrode active material, it is desirable to set to 10 micrometers or less ***** which kept the cycle life of a lithium secondary battery long. Five more micrometers or less are desirable, and 1 micrometer or less is more desirable. The above-mentioned particle is laid under the carbonaceous material, and the particle with which the front face was completely covered by the carbonaceous material, and the particle which has exposed the part to the exterior of a carbonaceous material exist. The part may be exposed to the exterior of a carbonaceous material although it is desirable that a particle front face is completely covered by the carbonaceous material. Moreover, in one particle of a negative-electrode active material, one piece or two or more above-mentioned particles which were laid under the carbonaceous material exist. If it is laid under the carbonaceous material even if many above-mentioned particles exist especially, it will not become a property top problem. It is desirable that graphite carbon or its floc has adjoined and adhered to the oxide particle. A charge-and-discharge property improves by having such structure. As for this, the graphite is more advantageous to diffusion of Li than amorphous carbon, and it can maintain the property which was excellent in the oxide, and can control cycle degradation.

[0016] The oxide particle of the preceding paragraph story which performs a mechanical pressure welding may not be a particle with the above-mentioned gestalt. By repeating a mechanical pressure welding, particle size becomes small and a predetermined particle size can be attained. The above-mentioned negative-electrode active material condition can be judged by observing the cross section of a negative-electrode active material with a scanning electron microscope (SEM). It asked for the particle size of the particle which can form Li and a compound by measuring the particle size distribution of the above-mentioned particle observed in the cross section of a negative-electrode active material. At this time, the number of each negative-electrode active materials of the number of the measured above-

mentioned particle was 500-1500. Moreover, if it is checked by cross-section observation of a negative-electrode active material that a carbonaceous material exists in the perimeter of the above-mentioned particle, it can be judged that the above-mentioned particle is laid under the carbonaceous material. In the negative-electrode active material of this invention, existence of a carbonaceous material was checked around the above-mentioned particle.

[0017] As for the content rate of the above-mentioned particle in the active material with which the above-mentioned particle was laid under the carbonaceous material, 0.95 or less [0.05 or more] are desirable at a weight ratio, 0.90 or less [further 0.10 or more] are desirable, 0.80 or less [0.20 or more] are desirable, and 0.75 especially or less [0.30 or more] are desirable.

[0018] As for the carbonaceous material under which said particle is laid, the crystalline carbon field must be included. Although said particle can be laid under the carbonaceous material which consists only of amorphous carbon, compared with crystalline carbon, the charge-and-discharge property is inferior. As for a crystalline carbon field, d_{002} is 0.3350nm or more 0.3650nm or less. CuK alpha rays, the tube voltage of 50kV, and the X-ray of 250mA of tube electric currents are used for the X-ray diffraction method of this invention, and it is 0.002 -0.01deg. It measured at the step. (002) The diffraction curve which is equivalent to diffraction from a field was graduated, the background was deleted, and the diffraction (002) correction curve of parenchyma was obtained. The peak of this correction curve sets the angle of diffraction of a field (002) to theta, and is expressed with 2θ . d_{002} was calculated from the bottom type.

[0019] $d_{002} = \lambda / (2 \sin \theta)$

Although a diffraction (002) peak separates into plurality depending on $\lambda = 0.15418\text{nm}$ carbonaceous material, d_{002} corresponding to a peak with the maximum reinforcement must be 0.3350nm or more 0.3650nm or less.

[0020] On the other hand, the magnitude (L_c) of the microcrystal of the direction of a c-axis is called for using the following formulas from the above-mentioned correction curve.

[0021] $L_c = K \cdot \lambda / (\beta \cdot \cos \theta)$

$K = 0.9$ $\lambda = 0.15418\text{nm}$ β : Half peak width (radian)

L_c calculated from the above-mentioned correction curve is 0.5nm. The above is desirable, 1 morenm or more 100nm or less is desirable, 5nm or more 80nm or less is more desirable, and 10 morenm or more 60nm or less is desirable. 15nm or more especially 50nm or less is desirable.

[0022] As for both carbonaceous materials, it is more desirable for the carbon of crystallinity and amorphous nature to exist. Wavelength of 0.5145nm A difference produces the Raman spectrum distribution using an argon laser by the crystallinity of a carbonaceous material. The c-th page corresponds to a laminating and the formed crystal structure, and, as for the peak of the 1580cm⁻¹ neighborhood, the peak of the 1360cm⁻¹ neighborhood is equivalent to the disordered amorphous structure. The peak of the 1580cm⁻¹ neighborhood is a peak in the range of 1570-1620cm⁻¹, the peak of the 1360cm⁻¹ neighborhood is a peak in the range of 1570-1620cm⁻¹, and the peak of the 1360cm⁻¹ neighborhood is a peak in the range of 1350-1370cm⁻¹. The peak intensity ratio [as opposed to / when the rate of crystalline carbon increases compared with amorphous carbon / the peak intensity of 1580cm⁻¹ near / an argon laser Raman spectrum] (R value) of the 1360cm⁻¹ neighborhood becomes small, and if the rate of amorphous carbon increases, it will become large. However, since an initial property will deteriorate if the rate of amorphous carbon increases, as for the rate of crystalline carbon and amorphous carbon, it is desirable that R values are 0.15-2.0. Especially, 0.3-1.2 are desirable.

[0023] Although crystalline carbon and amorphous carbon are used, as for the carbon particle of the preceding paragraph story which performs a mechanical pressure welding, it is more desirable that it is crystalline carbon. Since the negative-electrode active material which has predetermined physical properties especially as it is a carbon particle with a small particle size and a large specific surface area cannot be obtained, below 100m²/g of the specific surface area of the above-mentioned carbon particle is desirable, and its further 0.5-50m²/g are desirable. Moreover, for said carbon particle, d_{002} is 0.3350-. It is desirable that it is 0.3370nm.

[0024] Although difficulty graphitization precursors, such as easily-graphitizable precursors, such as a

petroleum pitch and a coal pitch, or an isotropic pitch, the poly acrylic nitril, phenol resin, and furan resin, are used, the easily-graphitizable precursor of a carbon precursor is more desirable in respect of conductivity or an initial property.

[0025] If specific surface area becomes large, irreversible capacity will increase a negative-electrode active material, and if it becomes small, the spreading engine performance will get worse. For this reason, 1-100m² / g of specific surface area are desirable, and its 2-50m² / g are more desirable especially.

[0026] As positive active material, multiple oxides, such as lithium cobalt oxide (Li_xCoO₂), a lithium nickel oxide (Li_xNiO₂), a lithium manganic acid ghost (Li_xMn₂O₄, Li_xMnO₃), and lithium nickel cobalt oxide (Li_xNi_yCo(1-y)O₂), can be used. here -- 0<=x<=1.2 and 0<=y<=1 it is . That is, although stoichiometric composition is sufficient as these, you may be the oxide [stoichiometric composition] slightly shifted. These matter has the desirable mean particle diameter of 3-40 micrometers.

[0027] The organic solvent in which the electrolytic solution dissolved lithium salt as an electrolyte is used. As an organic solvent, for example Butylene carbonate, propylene carbonate, diethyl carbonate, ethyl methyl carbonate, ethylene carbonate, dimethyl carbonate, methyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, ethoxy methoxyethane, gamma-butyl lactone, gamma-valerolactone, dipropyl carbonate, a tetrahydrofuran, Organic solvents, such as 2-methyl tetrahydrofuran, dioxane, dimethyl sulfoxide, a sulfolane, a methyl sulfolane, an acetonitrile, methyl acetate, and formic acid methyl, or two or more sorts of these mixed solvents are used.

[0028] As an electrolyte, lithium salt, such as a 6 phosphorus-fluoride acid lithium (LiPF₆), hoe lithium fluoride (LiBF₄), lithium perchlorate (LiClO₄), a bis-trifluoromethylsulfonyl imide lithium (LiN₂(CF₂SO₂)), a 6 fluoride arsenic lithium (LiAsF₆), and a trifluoro meta-sulfonic-acid lithium (LiCF₂SO₃), is used. Especially, a 6 phosphorus-fluoride acid lithium (LiPF₆), hoe lithium fluoride (LiBF₄), lithium perchlorate (LiClO₄), and a bis-trifluoromethylsulfonyl imide lithium (LiN₂(CF₂SO₂)) are desirable. The amount of dissolutions of the electrolyte to an organic solvent has desirable 1. in 0.5-2 mols /.

[0029] As electric conduction material of a positive electrode and a negative electrode, a graphite and the carbon with which amorphous or these are intermingled can be used. 1-300m²/g is desirable as mean particle diameter at 30 micrometers or less and specific surface area. Moreover, a carbon staple fiber with a diameter [of 0.1-10 micrometers] and a die length of 2-30 micrometers may be used. In order to maintain higher conductivity, as for especially the negative-electrode active material of this invention, it is desirable to use a graphite as electric conduction material or an active material, i.e., to consider as the mixed negative electrode of the negative-electrode active material of this invention and a graphite. At this time, a graphite may mix not only one sort but two or more sorts. On the other hand, metal particles with small reactivity with the electrolytic solution can also be used as electric conduction material. For example, it is the alloy which contains nickel, Co, Fe, Cu, Ti, Cr, and these in a negative electrode, and is the alloy which contains nickel, Co, Fe, Ti, Cr, aluminum, and these in a positive electrode. It is difficult for these metal particles to make a particle transform with a press, and since spreading nature will worsen if particle size becomes large, 30 micrometers or less of mean particle diameter are desirable.

[0030] Binding material bears the role which makes a charge collector connect with an active material and electric conduction material. Resin, such as polyvinylidene fluoride (PVDF), an ethylene-propylene-diene copolymer (EPDM), polytetrafluoroethylene (PTFE), polyethylene, polypropylene, polystyrene, polyvinyl pyridine, chlorosulfonated polyethylene, and a latex, can be used for binding material. Moreover, as for binding material, it is desirable that it is 2 - 20 % of the weight among the mixtures with which an active material, electric conduction material, and binding material were doubled. Especially a negative electrode has [the binding material of a positive electrode] 5 - 15 more desirable % of the weight two to 10% of the weight.

[0031] In a negative electrode, as for a charge collector, the foil or sponge metal made from Cu, nickel, or stainless steel is used. Moreover, in a positive electrode, the foil or sponge metal made from aluminum, nickel, or stainless steel is used. Generally, the combination of the negative-electrode charge

collector made from Cu and the positive-electrode charge collector made from aluminum is liked. Although reinforcement is [direction] high, and these foils are rolling foils and are desirable, they may be electrolysis foils. Moreover, the thickness of a foil has desirable 100 micrometers or less, and its 8-40 micrometers are especially desirable.

[0032] The ion conductivity of the electrolytic solution is low resistance, a separator does not have reactivity with the electrolytic solution, and sheet-like the thing or polymer electrolyte which is excellent in solution holdout is used. The nonwoven fabric which consists of porous membrane, a glass fiber, and the above-mentioned macromolecules, such as polypropylene, polyethylene, polyolefine, polyester, polytetrafluoroethylene, and Pori Flon, can be used for a sheet-like separator. Especially, porous **** made from polypropylene, polyethylene, and polyolefine is desirable. The polymer electrolyte which graft-ized ionic dissociation radicals, such as complex which the polymer electrolyte made the polymer matrix polyethylene oxide, polypropylene oxide, polyvinylidene fluoride, polyacrylamide, etc., and dissolved said electrolyte into the polymer matrix or a gel bridge formation object which contains a solvent further, low-molecular-weight polyethylene oxide, and crown ether, to the polymer principal chain, and the gel polymer electrolyte which made the macromolecule polymer contain said electrolytic solution are used.

[0033] In order to perform a mechanical pressure welding to a carbonaceous particle and an oxide particle, it is required to apply external force which the above-mentioned particles stick, and the equipment which is made to produce such behavior and is closed is used. the equipment which can perform a mechanical pressure welding like the ball mill equipment of a planet mold as the above-mentioned equipment in the case of the collision of a ball, a vessel wall, or balls, the container set as the predetermined gap, and the object for pressure weldings -- the equipment which can perform a mechanical pressure welding between knives can be used. By using the above-mentioned equipment, a mechanical pressure welding can be repeated for a carbonaceous particle and an oxide particle, and said particle can be laid under the carbonaceous material. At this time, if pressure-welding processing of long duration is performed, specific surface area will increase by leaps and bounds. However, laying [of said particle to a carbonaceous material] underground becomes being a short time inadequate, and it becomes the cause that a good property is lost. After repeating a mechanical pressure welding, it can heat-treat at the temperature of further 700-1200 degrees C. Although it is not necessary to carry out the above-mentioned heat treatment, it is desirable to heat-treat at 900-1100 degrees C especially 700-1200 degrees C. As long as the ambient atmosphere at this time is an ambient atmosphere which can prevent oxidation, it may be any in inert gas, nitrogen gas, and a vacuum.

[0034] After mixing solvents, such as a carbon precursor, an oxide particle, and a tetrahydrofuran, stirring and flowing back, the laying-under-the-ground processing by the carbon precursor removes a solvent at a desiccation process, and is carried out by carrying out carbonization processing at predetermined temperature. Especially the carbonization processing temperature of a carbon precursor has desirable 900-1200 degrees C 800-1500 degrees C. Moreover, a carbonization processing ambient atmosphere has the desirable inside of inert gas or nitrogen gas.

[0035] Although itself can be used for the active material which made the oxide particle lay under the carbonaceous material by pressure-welding processing or further heat treatment as a negative-electrode active material, the active material which went via the above-mentioned pressure-welding processing has a comparatively high specific surface area. For this reason, improvement in a property can be aimed at by mixing with a carbon precursor further and carrying out carbonization processing at the temperature of 800-1500 degrees C. Carbonization processing temperature here also has especially desirable 900-1200 degrees C 800-1500 degrees C. Moreover, a carbonization processing ambient atmosphere has the desirable inside of inert gas or nitrogen gas.

[0036] The lithium secondary battery of this invention consists of cell containers which sealed an electrode object, the electrolytic solution, and the electrode object and the electrolytic solution that carried out the **** laminating of the separator between the positive electrode which consists of positive active material, positive-electrode electric conduction material, a binder, and a positive-electrode charge collector, and a negative-electrode active material, a binder, a negative-electrode

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charge collector or the negative electrode that added negative-electrode electric conduction material further, and were connected with the electrode object. After an electrode object carries out the laminating of a positive electrode, a separator, and the negative electrode, carries out the laminating of each electrode of the structure which carried out the laminating of each strip-of-paper-like electrode which connected the tab, and wound it even if it was the structure which picked out the tab from each electrode, or the shape of a strip of paper which connected the tab and winds, it may be the structure made to deform flatly. that is, it is **** about a separator between the positive electrodes and negative electrodes which counter -- what is necessary is just a cell with an electrode object

[0037] This invention contains the invasion desorption nature particle which consists of either [at least] metal particles which raise the invasion desorption nature of said lithium ion between said positive electrodes and negative electrodes to said carbonaceous material at the time of a carbonaceous-material particle and charge and discharge, or a metallic-oxide particle. While having the end of composite powder this invasion desorption nature particle was embedded 50% of the weight or more in said carbonaceous-material particle As for 5 micrometers or less and 90 % of the weight or more, said invasion desorption nature particle has mean particle diameter in the negative-electrode material for lithium secondary batteries characterized by having the particle size of 10 micrometers or less, or 90 % of the weight or more having the particle size of 50 micrometers or less said end of composite powder.

[0038] This invention contains the invasion desorption nature particle which consists of either [at least] metal particles which raise the invasion desorption nature of said lithium ion between said positive electrodes and negative electrodes to said graphite at the time of a graphite particle and charge and discharge, or a metallic-oxide particle. This invasion desorption nature particle has the end of composite powder 50 % of the weight or more was embedded in said graphite particle, and, as for said graphite particle, a hexagonal crystal has 80 % of the weight or more and a rhombohedral crystal in 20 or less % of the weight of the negative-electrode material for lithium secondary batteries which comes out on the other hand at least, and is characterized by a certain thing.

[0039] As graphite powder concerning this invention, a natural graphite and an artificial graphite are used and especially a scale-like natural graphite is desirable.

[0040] Moreover, as a processing machine which grinds a raw material graphite in particle size of 100 micrometers or less, a jet mill is desirable. This is because the amount of generation of amorphous carbon decreases.

[0041] By the method of grinding to the ground graphite powder, the graphite of rhombohedral structure is ***** about 30%. It is desirable to make 2000 degree C or more of ***** 10% or less in this invention by being able to reduce the rate of rhombohedral structure by heat-treating this raw material powder above 900 degrees C, and heating the 3rd day or more above 2700 degrees C especially more preferably. It is desirable to perform heating under inert-gas-izing or a vacuum.

[0042] Moreover, a thing with few the amount is obtained in ***** in hexagonal by processing in the acidic solution containing at least one chosen from the groups which consist of a sulfuric acid, a nitric acid, perchloric acid, a phosphoric acid, and fluoric acid, rinsing, neutralizing the graphite powder obtained by grinding, and drying as well as ****.

[0043] the nonaqueous electrolyte rechargeable battery of this invention -- the conventional rechargeable battery -- comparing -- high-capacity-izing -- reinforcement can be carried out.

[0044] The lithium secondary battery of this invention is used for the power source of various pocket electronic equipment or an electrical machinery and apparatus. Especially A notebook sized personal computer, a note type word processor, a palm top A personal computer, a cellular phone, PHS, pocket facsimile, a pocket printer, a headphone stereo, a video camera, pocket television, portable CD, portable MD, an electric shaver, electronic ****, a transceiver, a power tool, radio, a tape recorder, a digital camera, (Pocket) It is used for the accumulation-of-electricity system for electric vehicle and also hybrid car and automatic vending machines, electric cart, and load leveling, a home capacitor, a distributed stationary-energy-storage machine system (it builds in deferment mold electric appliances), an emergency power distribution system, etc. [, such as a pocket copy machine and a handheld game machine,]

[0045] As for the lithium secondary battery of this invention, it is desirable that the safeguard for overcharge and overdischarge is prepared.

[0046]

[Embodiment of the Invention] (Example 1) The amorphous SiO particle with a mean particle diameter of 10 micrometers and the natural-graphite particle with a mean particle diameter of 20 micrometers were blended by the weight ratio 70:30, and ball mill processing which repeats a mechanical pressure welding for this with planet mold ball mill equipment was performed for 12 hours. A ball mill container and a ball with a diameter of 10mm are the products made from stainless steel, and powder adjustment and a ball mill were performed in Ar ambient atmosphere. Furthermore, 1100 degrees C and heat treatment of 1 hour were performed in Ar ambient atmosphere. As a result of analyzing the end of SiO-graphite composite powder it was obtained by this with a wide angle X-ray diffraction method, d002 of a graphite was 0.3358nm. Moreover, Lc was 45nm. Moreover, the R value was 0.5. As a result of observing the cross section in the above-mentioned end of composite powder, a SiO particle is laid underground in a graphite particle and the mean particle diameter of SiO is 1.2 micrometers. 95% or more of the whole was 10 micrometers or less. Moreover, 63m² / g, and 95% or more of the specific surface area in the end of SiO-graphite composite powder was 40 micrometers or less. The end of SiO-graphite composite powder :P N-methyl pyrrolidone solution of PVDF and the end of Si-graphite composite powder were kneaded so that it might become the weight ratio of VDF=85:15, and it applied to Cu foil with a thickness of 20 micrometers. Pressurization molding of the electrode was carried out after 1-hour desiccation and with a roller press at 120 degrees C, and finally this was pierced in diameter of 20mm, and was made into the negative electrode. In addition, the amorphous carbonization object is contained in the graphite about 3%.

[0047] The powder of LiCoO₂ with a mean particle diameter of 10 micrometers was used for positive active material. LiCoO₂ powder: Graphite :P It mixed so that it might become the weight ratio of VDF=90:6:4, and the slurry was formed. N-methyl pyrrolidone solution as well as [at this time] a negative electrode was used. This slurry was fully applied to aluminum foil with a thickness of 20 micrometers after kneading. Pressurization molding of the electrode was carried out after 1-hour desiccation and with a roller press at 120 degrees C, and finally this was pierced in diameter of 20mm, and was made into the positive electrode. here -- since the capacity of a negative electrode is large -- a negative electrode -- the positive electrode to a mixture -- the weight ratio of a mixture was set to 7.

[0048] The coin mold cell which shows an above-mentioned negative electrode and an above-mentioned positive electrode to drawing 1 was constituted, and the property was evaluated. the positive-electrode can 1 made from stainless steel -- positive-electrode charge collector 2a and a positive electrode -- a mixture -- the positive electrode 2 which consists of 2b was installed by spot welding. moreover, the negative-electrode can 3 made from stainless steel -- negative-electrode charge collector 4a and a negative electrode -- the negative electrode 4 which consists of mixture 4b was installed by spot welding. In both a positive electrode and a negative electrode, it is one mol [1.] LiPF₆ to the mixed solvent of 1:2 of ethylene carbonate (EC) and dimethyl carbonate (DMC). Infiltrated the dissolved electrolytic solution, the positive electrode and the negative electrode were made for the separator 5 made from polyethylene to counter by ****, and the positive-electrode can and the negative-electrode can were stuck by pressure with the insulating gasket 6.

[0049] This cell is charged by 1mA of charging currents, and charge termination electrical-potential-difference 4.2V, and it is 1mA of discharge currents, and discharge-final-voltage 2.7V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell -- 7.3mAh(s) it is -- the percentage of irreversible capacity was 23%. On the other hand; the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 87%.

[0050] (Example 2) The amorphous SiO particle with a mean particle diameter of 10 micrometers and the natural-graphite particle with a mean particle diameter of 20 micrometers were blended by the weight ratio 80:20, and ball mill processing was performed for this with the same planet mold ball mill equipment as an example 1 for 48 hours. Powder adjustment and a ball mill were performed in Ar ambient atmosphere. the result of having analyzed the end of SiO-graphite composite powder it was

obtained by this with the wide angle X-ray diffraction method -- d_{002} of a graphite -- 0.3367nm it was . Moreover, L_c was 30nm. moreover, an R value -- 0.8 it was . As a result of observing the cross section in the above-mentioned end of composite powder, a SiO particle is laid underground in a graphite particle and the mean particle diameter of SiO is 0.8 micrometers. 98 % of the weight or more was 10 micrometers or less. Moreover, 49m² / g, and 98 % of the weight or more of the specific surface area in the end of SiO-graphite composite powder were 40 micrometers or less.

[0051] The tetrahydrofuran was mixed with the above-mentioned end of SiO-graphite composite powder, and a petroleum pitch by the weight ratio of 100:30:300, and it stirred and flowed back for 1 hour. The tetrahydrofuran was removed using the rotary evaporator, the vacuum drying of this was carried out at 150 degrees C for 3 hours, and /pitch composite material was obtained in the end of SiO-graphite composite powder. This composite material is cracked to 200 or less meshes by the cutter mill, and, subsequently they are 3 degrees C / min in air. At the rate, to 250 degrees C, the temperature up was carried out and it held for 1 hour. The temperature up of this was carried out to 1100 degrees C by h in 20 degrees C /under nitrogen circulation, it held for 1 hour, and the pitch was carbonized. This was cracked to 200 or less meshes by the cutter mill, and the end of SiO-graphite-pitch composite powder was obtained. As a result of an X diffraction's analyzing the end of SiO-pitch composite powder it was obtained, d_{002} of a graphite is 0.3368nm. Two 0.3435nm peaks were observed. Moreover, the R value was 1.0. Moreover, the specific surface area in the end of SiO-graphite-pitch composite powder was 28m² / g. Moreover, amount detection of Si and the SiC was carried out a little by heating at 1100 degrees C.

[0052] The cell which used the above-mentioned end of SiO-pitch composite powder for the negative-electrode active material was produced by the same approach as an example 1. However, the positive-electrode ingredient used LiNi_{0.8}Co_{0.2}O₂ with a mean particle diameter of 10 micrometers. Here, the electrolytic solution is one mol [/l.] LiPF₆ to the mixed solvent of EC, DMC, and DEC3:6:1. The dissolved electrolytic solution was used.

[0053] It is 1mA of charging currents, and charge termination electrical-potential-difference 4.15V about this cell. It charges and is 1mA of discharge currents, and discharge-final-voltage 2.8V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell -- 6.8mAh(s) it is -- the percentage of irreversible capacity was 13%. On the other hand, the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 92%.

[0054] (Example 3) crystallinity with a mean particle diameter of 20 micrometers -- SnO₂ The particle and the natural-graphite particle with a mean particle diameter of 10 micrometers were blended by the weight ratio 50:50, and planet mold ball mill processing was performed for 6 hours. A ball mill container and a ball with a diameter of 10mm are the products made from stainless steel, and powder adjustment and a ball mill were performed in Ar ambient atmosphere. Furthermore, it gave at 900 degrees C and heat-treated in Ar for 5 hours. the result of having analyzed the end of SnO₂-graphite composite powder it was obtained by this with the wide angle X-ray diffraction method -- d_{002} of carbon -- 0.3355nm it was . Moreover, L_c was 60nm. Moreover, the R value was 0.4. As a result of observing the cross section in the above-mentioned end of composite powder, it is laid underground in a graphite particle and SnO₂ particle is SnO₂. Mean particle diameter was 2.3 micrometers. Moreover, the specific surface area in the end of SnO₂-graphite composite powder was 43m² / g.

[0055] The slurry was produced so that it might become the weight ratio of 45:45:10 about graphite powder with an above-mentioned end [of SnO₂-graphite composite powder], and a mean particle diameter of 15 micrometers, and PVDF, this was fully kneaded and the negative electrode was produced by the same approach as an example 1. Moreover, the coin mold cell was produced by the same approach as an example 1. However, the positive-electrode ingredient used LiMn₂O₄ with a mean particle diameter of 10 micrometers.

[0056] This cell is charged by 1mA of charging currents, and charge termination electrical-potential-difference 4.3V, and it is 1mA of discharge currents, and discharge-final-voltage 2.8V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell -- 4.2mAh(s) it is -- the percentage of irreversible capacity was 17%. On the other hand, the

discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 94%.

[0057] (Example 4) Amorphous SnSiO_3 with a mean particle diameter of 10 micrometers The particle and the natural-graphite particle with a mean particle diameter of 10 micrometers were blended by the weight ratio 80:20, and the same ball mill processing as an example 1 was performed for 150 hours. A ball mill container and a ball are the products made from stainless steel, and powder adjustment and a ball mill were performed in Ar ambient atmosphere. The tetrahydrofuran was mixed with the above-mentioned end of SnSiO_3 -graphite composite powder, and a coal pitch by the weight ratio of 100:30:300, and it stirred and flowed back for 1 hour. The tetrahydrofuran was removed using the rotary evaporator, the vacuum drying of this was carried out at 150 degrees C for 3 hours, and /pitch composite material was obtained in the end of germanium-graphite composite powder. This composite material is cracked to 200 or less meshes by the cutter mill, and, subsequently they are 3 degrees C / min in air. At the rate, to 350 degrees C, the temperature up was carried out and it held for 1 hour. The temperature up of this was carried out to 1000 degrees C by h in 20 degrees C /under nitrogen circulation, it held for 1 hour, and the pitch was carbonized. This was cracked to 200 or less meshes by the cutter mill, and the end of SnSiO_3 -pitch composite powder was obtained. As a result of analyzing the end of SnSiO_3 -pitch composite powder it was obtained with a wide angle X-ray diffraction method, d002 of carbon was 0.3398nm. The mean particle diameter of SnSiO_3 calculated from cross-section observation was 0.6 micrometers. Moreover, the R value was 1.0. Moreover, the specific surface area in the end of SnSiO_3 -pitch composite powder was $24\text{m}^2/\text{g}$. SnSiO_3 The particle was embedded in the graphite particle and 99 % of the weight or more was 10 micrometers or less.

[0058] The cell which used the above-mentioned end of SnSiO_3 -pitch composite powder for the negative-electrode active material was produced by the same approach as an example 1. However, for the electrolytic solution, PC and DMC are 1.2 mols [l.] LiPF_6 to the mixed solvent of 2:3. The dissolved electrolytic solution was used.

[0059] This cell is charged by 1.5mA of charging currents, and charge termination electrical-potential-difference 4.2V, and it is 1.5mA of discharge currents, and discharge-final-voltage 2.7V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell - 4.1mAh(s) it is -- the percentage of irreversible capacity was 15%. On the other hand, the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 93%.

[0060] (Example 5) Amorphous SnSiO_3 with a mean particle diameter of 10 micrometers The particle and the natural-graphite particle with a mean particle diameter of 20 micrometers were blended by the weight ratio 30:70, and the same ball mill processing as an example 1 was performed for 48 hours. Powder adjustment and a ball mill were performed in Ar ambient atmosphere. The tetrahydrofuran was mixed with the above-mentioned end of SnSiO_3 -graphite composite powder, and a petroleum pitch by the weight ratio of 100:70:700, and it stirred and flowed back for 1 hour. The tetrahydrofuran was removed using the rotary evaporator and the vacuum drying of this was carried out at 150 degrees C for 3 hours. This composite material is cracked to 200 or less meshes by the cutter mill, and, subsequently they are 3 degrees C / min in air. At the rate, to 350 degrees C, the temperature up was carried out and it held for 1 hour. The temperature up of this was carried out to 1100 degrees C by h in 20 degrees C /under nitrogen circulation, it held for 1 hour, and the pitch was carbonized. This was cracked to 200 or less meshes by the cutter mill, and the end of SnSiO_3 -graphite-pitch composite powder was obtained. As a result of analyzing the end of SnSiO_3 -graphite-pitch composite powder it was obtained with a wide angle X-ray diffraction method, d002 of a graphite was 0.3361nm and 0.3378nm. SnSiO_3 calculated from cross-section observation Mean particle diameter was 2.2 micrometers. Moreover, the R value was 1.3. Moreover, the specific surface area in the end of SnSiO_3 -graphite-pitch composite powder was $20\text{m}^2/\text{g}$.

[0061] The cell which used the above-mentioned end of SnSiO_3 -pitch composite powder for the negative-electrode active material was produced by the same approach as an example 1. However, for the electrolytic solution, EC and DMC are 1.5 mols [l.] LiPF_6 to the mixed solvent of 1:2. The

dissolved electrolytic solution was used.

[0062] This cell is charged by 1mA of charging currents, and charge termination electrical-potential-difference 4.2V, and it is 1mA of discharge currents, and discharge-final-voltage 2.7V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell -- 3.5mAh(s) it is -- the percentage of irreversible capacity was 9%. On the other hand, the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 95%.

[0063] (Example 6) The tetrahydrofuran was mixed with the amorphous SiO particle of 1 micrometer of mean diameters, and the petroleum pitch by the weight ratio of 100:50:500, and it stirred and flowed back for 1 hour. The tetrahydrofuran was removed using the rotary evaporator, the vacuum drying of this was carried out at 150 degrees C for 3 hours, and /pitch composite material was obtained. This composite material is cracked to 200 or less meshes by the cutter mill, and, subsequently they are 3 degrees C / min in air. At the rate, to 250 degrees C, the temperature up was carried out and it held for 1 hour. The temperature up of this was carried out to 900 degrees C by h in 20 degrees C /under nitrogen circulation, it held for 1 hour, and the pitch was carbonized. This was cracked to 200 or less meshes by the cutter mill, and the end of SiO-carbon composite powder was obtained. the result of having analyzed the end of SiO-carbon composite powder it was obtained with the wide angle X-ray diffraction method - d002 of carbon -- 0.3610nm it was . Moreover, Lc was 5nm. Moreover, the R value was 1.4. Moreover, the specific surface area in the end of SiO-carbon composite powder is 7m2 / g, and the SiO particle was embedded in the carbon particle.

[0064] The cell which used the above-mentioned end of SiO-carbon composite powder for the negative-electrode active material was produced by the same approach as an example 1. However, for the electrolytic solution, EC and DMC are 1.0 to the mixed solvent of 1:2. LiPF6 of a mol/liter The dissolved electrolytic solution was used.

[0065] This cell was charged by 1mA of charging currents, and charge termination electrical-potential-difference 4.2V, and 1mA of discharge currents and the charge-and-discharge cycle trial made to discharge by discharge-final-voltage 2.7V were carried out. consequently, the initial discharge capacity of a cell -- 7.2mAh(s) it is -- the percentage of irreversible capacity was 20%. On the other hand, the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 88%.

[0066] (Example 1 of a comparison) The tetrahydrofuran was mixed with the amorphous SiO particle of 1 micrometer of mean diameters, and the petroleum pitch by the weight ratio of 100:50:500, and it stirred and flowed back for 1 hour. The tetrahydrofuran was removed using the rotary evaporator, the vacuum drying of this was carried out at 150 degrees C for 3 hours, and /pitch composite material was obtained. This composite material is cracked to 200 or less meshes by the cutter mill, and, subsequently they are 3 degrees C / min in air. At the rate, to 250 degrees C, the temperature up was carried out and it held for 1 hour. The temperature up of this was carried out to 700 degrees C by h in 20 degrees C /under nitrogen circulation, it held for 1 hour, and the pitch was carbonized. This was cracked to 200 or less meshes by the cutter mill, and the end of SiO-pitch composite powder was obtained. the result of having analyzed the end of SiO-pitch composite powder it was obtained with the wide angle X-ray diffraction method - d002 of carbon -- 0.3691nm it was . Moreover, the R value was 1.7. Moreover, the specific surface area in the end of SiO-pitch composite powder was 7m2 / g.

[0067] The cell which used the above-mentioned end of Si-carbon composite powder for the negative-electrode active material was produced by the same approach as an example 1. However, for the electrolytic solution, EC and DMC are 1.0 to the mixed solvent of 1:2. LiPF6 of a mol/liter The dissolved electrolytic solution was used.

[0068] This cell is charged by 1mA of charging currents, and charge termination electrical-potential-difference 4.2V, and it is 1mA of discharge currents, and discharge-final-voltage 2.7V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell -- 7.8mAh(s) it is -- the percentage of irreversible capacity was 45%. On the other hand, the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 56%.

[0069] (Example 2 of a comparison) crystallinity with a mean particle diameter of 10 micrometers -- SnO2 The slurry was produced so that it might become the weight ratio of 30:60:10 about natural-

graphite powder with a mean particle diameter of 15 micrometers and PVDF, this was fully kneaded and the negative electrode was produced by the same approach as an example 1. Moreover, the coin mold cell was produced by the same approach as an example 1. However, the positive-electrode ingredient used LiMn_2O_4 with a mean particle diameter of 10 micrometers.

[0070] This cell is charged by 1mA of charging currents, and charge termination electrical-potential-difference 4.3V, and it is 1mA of discharge currents, and discharge-final-voltage 2.8V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell - 3.7mAh(s) it is - the percentage of irreversible capacity was 36%. On the other hand, the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 20%.

[0071] (Example 7) The cylindrical lithium secondary battery was produced as a lithium secondary battery of this invention. The basic configuration is shown in drawing 2. an electrode object - the positive-electrode charge collector 11 - a positive electrode - the positive electrode 13 and the negative-electrode charge collector 14 which come to apply a mixture 12 - a negative electrode - it consists of a negative electrode 16 which comes to apply a mixture 15, and a separator 17, and a laminating is carried out to the order of a positive electrode 13, a separator 17, a negative electrode 16, and a separator 17, and as shown in drawing 3, this is wound and it becomes. As for the positive electrode 13 of an electrode object, and the negative electrode 16, the positive-electrode tab 18 and the negative-electrode tab 19 are connected, respectively. This electrode object is contained by the cell can 20, and the cell can 20, the negative-electrode tab 19, and the cell lid 21 and the positive-electrode tab 18 are connected, respectively. It fixed to the cell can 20 through the insulating gasket 22, and the cell lid 21 has sealed the inside of an electrode object and the cell can 20. Moreover, in order to prevent contact on an electrode object, the cell can 20, or the cell lid 21, the electric insulating plate 23 is also formed. The electrolytic solution containing Li ion is poured in into the sealed cell can. The mild steel with which the cell can 20 and the cell lid 21 performed SUS304, SUS316, and corrosion-resistant coating is used.

[0072] The scale-like graphite with a mean particle diameter of 5 micrometers was used as LiCoO_2 with a mean particle diameter of 10 micrometers and positive-electrode electric conduction material, and aluminum foil with a thickness of 20 micrometers was used for positive active material as PVDF and a positive-electrode charge collector as a binder. LiCoO_2 , a scale-like graphite, and the weight ratio of PVDF - 88:7:5 - carrying out - N-methyl pyrrolidone - adding - mixing - a positive electrode - a mixture - the slurry was adjusted. This was applied to both sides of aluminum foil, and carried out the vacuum drying at 120 degrees C for 1 hour, and pressurization molding of the electrode was carried out with the roller press after that. Then, it started in width of face of 40mm, and die length of 285mm, and the positive electrode was produced. here - a part with a die length [of the both ends of a positive electrode] of 10mm - a positive electrode - the mixture was not applied but aluminum foil has exposed it. The negative-electrode tab made from nickel was stuck to one of these by pressure by ultrasonic jointing.

[0073] The negative-electrode active material was produced by the following approaches. The amorphous SiO particle with a mean particle diameter of 10 micrometers and the natural-graphite particle with a mean particle diameter of 20 micrometers were blended by the weight ratio of 80:20, and ball mill processing was performed for 48 hours. A ball mill container and a ball are the products made from stainless steel, and powder adjustment and a ball mill were performed in Ar ambient atmosphere. The tetrahydrofuran was mixed with the above-mentioned end of SiO -carbon composite powder, and a petroleum pitch by the weight ratio of 100:50:500, and it stirred and flowed back for 1 hour. The tetrahydrofuran was removed using the rotary evaporator, the vacuum drying of this was carried out at 150 degrees C for 3 hours, and the end of SiO -graphite-pitch composite powder was obtained. This composite material is cracked to 200 or less meshes by the cutter mill, and, subsequently they are 3 degrees C / min in air. At the rate, to 250 degrees C, the temperature up was carried out and it held for 1 hour. The temperature up of this was carried out to 1100 degrees C by h in 20 degrees C /under nitrogen circulation, it held for 1 hour, and the pitch was carbonized. This was cracked to 200 or less meshes by the cutter mill, and the end of SiO -pitch composite powder was obtained. The end of SiO -graphite-pitch

[0082] The negative-electrode active material produced the end of SiO-graphite-pitch composite powder like the example 7. Cu foil with a thickness of 20 micrometers was used as PVDF and a negative-electrode charge collector as the above-mentioned negative-electrode active material and a binder. They are a scale-like graphite with a mean particle diameter of 10 micrometers and the average diameter of

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0.2 micrometers as negative-electrode electric conduction material. Cu foil with a thickness of 20 micrometers was used as PVDF and a negative-electrode charge collector as a carbon fiber with an average die length of 30 micrometers and a binder. a negative-electrode active material, a scale-like graphite, a carbon fiber, and the weight ratio of PVDF -- 55:30:5:10 -- carrying out -- N-methyl pyrrolidone -- adding -- mixing -- a negative electrode -- a mixture -- the slurry was adjusted. This was applied to both sides of Cu foil with the doctor blade method, and it dried at 100 degrees C for 2 hours. A negative electrode has the shape of a 70x120mm strip of paper.

[0083] The (a) plan of a square shape lithium secondary battery and the (b) sectional view are shown in drawing 4. A dimension is 30mm in height of 100mm, width of face of 130mm, and depth outside this cell. The electrode object which carried out the laminating of a positive electrode 31 and the negative electrode 32 by turns into the separator 33 made from polyethylene processed into saccate was inserted in the cell can 34 made from aluminum. here -- a positive electrode -- a mixture and a negative electrode -- the weight ratio of a mixture was set to 5:1. The positive-electrode lead 35 and the negative-electrode lead 37 which were welded to the upper part of each electrode were connected to the positive-electrode terminal 38 and the negative-electrode terminal 39, respectively. The positive-electrode terminal 38 and the negative-electrode terminal 39 are inserted in the cell lid 41 through the packing 40 made from polypropylene. An external cable and a cell are connectable with the nut 50 attached in the positive-electrode terminal 38 and the negative-electrode terminal 39. Electrolytic-solution pouring-in opening was installed in the relief valve for emitting the gas accumulated in the interior of a cell to the cell lid 41, when the pressure inside a cell reaches four to 7 atmospheric pressure, and the list. A relief valve consists of the gas-evolution opening 42, O ring 43, and a closure bolt 44. Pouring-in opening consists of an inlet 45, O ring 46, and a closure bolt 47. After carrying out laser beam welding of the cell can 34 and the cell lid 41, the electrolytic solution was introduced from the inlet 45, the inlet 45 was sealed with the closure bolt 47, and the square shape lithium secondary battery was completed. For the used electrolytic solution, EC and DMC are LiPF₆ to the mixed solvent of 1:2. It is the solution in which one mol /was dissolved 1. The average discharge voltage of this cell is 3.4V, rated capacity 38Ah, and 130 Whs.

[0084] The cell lid 41 of the above-mentioned square shape lithium secondary battery 51 was turned up, it has arranged to the single tier so that a 100x130mm side face may counter, and 8 series connection group cells shown in drawing 5 were assembled. It inserted two 2x10x100mm spacers 52 made from Pori ethylene tetrafluoride at a time along the height direction between the opposed faces of a cell 51. The side face of a group cell, the metal plate 53 made from stainless steel attached in order, and the fixing component 58 made from Pori ethylene tetrafluoride were fixed with the bolt 59, and it bound tight so that a pressure might join the inside sense of a cell 51. The rib-like height 60 was made to form in the metal plate 53 made from stainless steel. It connected by the current cable so that all cells might become a series connection, and the positive-electrode terminal of each square shape cell 51 and the negative-electrode terminal were connected to the positive-electrode terminal 54 of a group cell, and the negative-electrode terminal 55. Furthermore, it connected with the control circuit substrate 56 through the positive-electrode volt input cable and the negative-electrode volt input cable, respectively, and the positive-electrode terminal of each cell 51 and the negative-electrode terminal measured the electrical potential difference and current of each cell for charge-and-discharge control of a group cell. When the control circuit substrate 56 has equipped with the microcomputer and the electrical potential difference of at least one cell 51 and one side of a current separate from it from a setting range, it has the function to stop the charge and discharge of a group cell. The thermocouple 57 was attached in the side face of the cell which is in the 4th location from an end, and when delivery and cell temperature exceeded laying temperature for a temperature signal to the control circuit substrate 56, it was made to stop charge and discharge. The average discharge voltage of a **** cell is 27.2V, rated capacity 38Ah, and 1030 Whs.

[0085] Although the electrode object was the laminating mold of a strip-of-paper-like electrode, even if it is flat and is an ellipse-like winding mold, the same group cell as this example can consist of this examples.

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the whole, the neighboring peak is decreasing 43.3 degrees which belongs to rhombohedral structure, and 46.0 degrees by any [900 degrees C and 2850 degrees C] heat-treatment as a result of the X diffraction of graphite powder, and the latter was [the former was about 15% and] about 7%. The remainder is substantially hexagonal. In addition, the amorphous carbonization object is contained in the graphite about 3%.

[0092] Moreover, in the case of 2850 degrees C, the amount of Si contained as an impurity in graphite powder decreased with 27 ppm whenever [1140 ppm and stoving temperature], when whenever [stoving temperature] was 900 degrees C.

[0093] Moreover, the jet mill ground the scale-like raw material graphite to 100 micrometers or less similarly. Then, this graphite powder was immersed for one day with the mixed acid of a sulfuric acid and a nitric acid. Then, washing by distilled water and neutralization by the still thinner sodium-hydroxide water solution were performed. Thus, what was obtained was dried at 120 degrees C, the neighboring peak decreased 43.3 degrees which belongs to rhombohedral structure, and 46.0 degrees as a result of the X diffraction, and the amount was 20% or less of the whole.

[0094] The composite powder end of 20% of SiO₂80%-graphites was obtained by weight using planet mold ball mill equipment using such graphite powder like the example 1. It was the same as that of an example 1 almost the end of composite powder.

[0095] Moreover, the end of composite powder was manufactured like the above-mentioned under nitrogen-gas-atmosphere mind using the graphite powder heat-treated for 4 hours - ten days at 2850 degrees C.

[0096]

[Table 1]

表 1

加熱処理時間	炭素体晶構造割合 (%)	リチウム吸蔵容量 (mAh/g)	リチウム放出容量 (mAh/g)
4時間	18.2	332	320
10時間	14.8	345	325
1日	13.8	343	334
3日	11.3	358	338
5日	9.7	368	351
10日	7.1	385	360

[0097] The rechargeable battery for an experiment for investigating a cell property, using these end of composite powder as a negative-electrode active material was manufactured.

[0098] two kinds of graphite powder whose above-mentioned heat-treatment is 900 degrees C or 2850 degrees C -- as a binder -- polyvinylidene fluoride (PVDF) -- 10wt(s)% -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a mixture -- the slurry was prepared. this mixture -- the slurry was applied to one side of copper foil with a thickness of 10 micrometers, and the vacuum drying was carried out at 120 degrees C after that for 1 hour. After the vacuum drying, with the roller press, pressurization molding of the electrode was carried out and thickness was made into the range of 85-90 micrometers. the mixture per unit area -- coverage -- an average of 10 mg/cm² it is -- it started in 10mmx10mm magnitude, and the electrode was produced.

[0099] The mixed solvent of the ethylene carbonate and diethyl carbonate of a volume ratio 1:1 and a 6 phosphorus-fluoride acid lithium are used for the electrolytic solution, and it is lithium concentration 1 mol/l. It carried out.

[0100] By energizing with a fixed current between an operation pole and a counter electrode, the occlusion and emission of a lithium carried out repeatedly, and examined the capacity at that time. Here, potential of the minimum of an operation pole and an upper limit was set to 0V and 5V, respectively.

[0101] It carried out by having repeated the occlusion and emission of a lithium, and the relation of the

occlusion and emission capacity, and electrode potential of a lithium to the 5th cycle eye from which those capacity would be in the steady state was investigated.

[0102] As the lithium secondary battery using these end of composite powder was shown in Table 1, lithium occlusion capacity and emission capacity were both 300 or more mAh/g per active material weight. That is, when rhombohedral structure used 20% or less and the graphite powder of little this invention, the negative electrode with a large capacity was obtained. Moreover, when heat-treatment was made high with 2850 degrees C, lithium occlusion capacity and emission capacity showed the larger value by using the graphite powder whose rhombohedron it is a high grade and is 20% or less.

[0103] Based on the above experimental result, the cylindrical lithium cell shown in drawing 2 was manufactured. as positive active material -- as LiCoO_2 and an electric conduction agent -- acetylene black -- as 7wt(s)% and a binder -- polyvinylidene fluoride (PVDF) -- 5wt(s)% -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a positive electrode -- the slurry of a mixture was prepared.

[0104] the same -- as a negative-electrode active material -- as the graphite powder of this invention, and a binder -- PVDF -- 10wt(s)% -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a negative electrode -- the slurry of a mixture was prepared.

[0105] a positive electrode -- the mixture was applied to both sides of aluminium foil with a thickness of 25 micrometers, and the vacuum drying was carried out at 120 degrees C after that for 1 hour. After the vacuum drying, with the roller press, pressurization molding of the electrode was carried out and thickness was set to 195 micrometers. the mixture per unit area -- coverage -- 55 mg/cm² It became, it started in width of face of 40mm, and magnitude with a die length of 285mm, and the positive electrode was produced. however, a part with a die length [of the both ends of a positive electrode] of 10mm -- a positive electrode -- a mixture was not applied, but aluminium foil is exposed, and the positive-electrode tab of one of these is stuck by pressure by ultrasonic jointing.

[0106] on the other hand -- a negative electrode -- the mixture was applied to both sides of copper foil with a thickness of 10 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour. After the vacuum drying, with the roller press, pressurization molding of the electrode was carried out and thickness was set to 175 micrometers. the mixture per unit area -- coverage -- 25 mg/cm² it is -- it started in width of face of 40mm, and magnitude with a die length of 290mm, and the negative electrode was produced. a positive electrode -- the same -- a part with a die length [of the both ends of *****] of 10mm -- a negative electrode -- a mixture was not applied, but copper foil was exposed, and the negative-electrode tab was stuck to one of these by pressure by ultrasonic jointing.

[0107] The micropore film with a thickness [of 25 micrometers] and a width of face of 44mm made from polypropylene was used for the separator. Superposition and this were wound in order of the positive electrode, the separator, the negative electrode, and the separator, and it considered as the electrode group. This was inserted in the cell can and the converging section for carrying out can bottom welding of the negative-electrode tab, and closing a positive-electrode lid was formed. A volume ratio is a 6 phosphorus-fluoride acid lithium to the mixed solvent of the ethylene carbonate and diethyl carbonate of 1:1 1 mol/l After pouring into a cell can the electrolytic solution in which it was made to dissolve and welding a positive-electrode tab to a positive-electrode lid, the positive-electrode lid was closed and the cell was produced.

[0108] Charge and discharge were repeated for 300mA of charge and discharge currents, and a charge-and-discharge termination electrical potential difference as 4.2V and 2.8V using this cell, respectively. Moreover, the charging current was changed in 300 to 900mA, and rapid charge and discharge were performed.

[0109] It carried out by having repeated charge and discharge about this lithium secondary battery, and change of the discharge capacity of a cell was investigated. Consequently, the highest discharge capacity was 683 mAh/g and the decreasing rate to the highest capacity of the discharge capacity in a 200 cycle eye was 86%.

[0110] Furthermore, as a result of investigating the charge and discharge current at the time of performing rapid charge and discharge, and the relation of discharge capacity, in 900mA of charge and discharge currents, discharge capacity is 573 mAh/g, the deduction coefficient of capacity to the

discharge capacity in 300mA of charge and discharge currents was 16%, respectively, the deduction coefficient of capacity has been improved 30% or more, and it was shown by using the graphite powder of this invention as a negative-electrode active material that the lithium secondary battery of this invention has the outstanding rapid charge-and-discharge property.

[0111] The lithium secondary battery which particle size excelled [rate / of 100 micrometers or less and rhombohedral structure] in the reversibility of the occlusion and release reaction of a lithium by using for the negative-electrode active material of a lithium secondary battery the end of lead powder which is 20% or less, and is a high energy consistency and was excellent in the rapid charge-and-discharge property is obtained.

[0112] (Example 11) The amorphous SiO particle with a mean particle diameter of 10 micrometers and the graphite particle with a mean particle diameter of 20 micrometers obtained in the example 10 were blended by the weight ratio 80:20, and ball mill processing was performed for this with the same planet mold ball mill equipment as an example 1 for 48 hours. Powder adjustment and a ball mill were performed in Ar ambient atmosphere. the result of having analyzed the end of SiO-graphite composite powder it was obtained by this with the wide angle X-ray diffraction method -- d002 of a graphite -- 0.3367nm it was . Moreover, Lc was 30nm. moreover, an R value -- 0.8 it was . As a result of observing the cross section in the above-mentioned end of composite powder, the SiO particle was laid underground in the graphite particle, the mean particle diameter of SiO was 0.8 micrometers, and 98 % of the weight or more was 10 micrometers or less. Moreover, 49m² / g, and 98 % of the weight or more of the specific surface area in the end of SiO-graphite composite powder were 40 micrometers or less.

[0113] The tetrahydrofuran was mixed with the above-mentioned end of SiO-graphite composite powder, and a petroleum pitch by the weight ratio of 100:30:300, and it stirred and flowed back for 1 hour. The tetrahydrofuran was removed using the rotary evaporator, the vacuum drying of this was carried out at 150 degrees C for 3 hours, and /pitch composite material was obtained in the end of SiO-graphite composite powder. This composite material is cracked to 200 or less meshes by the cutter mill, and, subsequently they are 3 degrees C / min in air. At the rate, to 250 degrees C, the temperature up was carried out and it held for 1 hour. The temperature up of this was carried out to 1100 degrees C by h in 20 degrees C /under nitrogen circulation, it held for 1 hour, and the pitch was carbonized. This was cracked to 200 or less meshes by the cutter mill, and the end of SiO-graphite-pitch composite powder was obtained. As a result of an X diffraction's analyzing the end of SiO-pitch composite powder it was obtained, d002 of a graphite is 0.3368nm. Two 0.3435nm peaks were observed. Moreover, the R value was 1.0. Moreover, the specific surface area in the end of SiO-graphite-pitch composite powder was 28m² / g.

[0114] The cell which used the above-mentioned end of SiO-pitch composite powder for the negative-electrode active material was produced by the same approach as an example 1. However, the positive-electrode ingredient used LiNi_{0.8}Co_{0.2}O₂ with a mean particle diameter of 10 micrometers. Here, the electrolytic solution is one mol [l.] LiPF₆ to the mixed solvent of EC, DMC, and DEC3:6:1. The dissolved electrolytic solution was used.

[0115] It is 1mA of charging currents, and charge termination electrical-potential-difference 4.15V about this cell. It charges and is 1mA of discharge currents, and discharge-final-voltage 2.8V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell -- 6.8mAh(s) it is -- the percentage of irreversible capacity was 13%. On the other hand, the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 92%.

[0116] (Example 12) Si with a mean particle diameter of 10 micrometers, germanium or aluminum particle, and the graphite particle with a mean particle diameter of 20 micrometers obtained in the example 10 were respectively blended by the weight ratio 50:50, and ball mill processing which repeats a mechanical pressure welding for this with planet mold ball mill equipment was performed for 24 hours. A ball mill container and a ball are the products made from stainless steel, and powder adjustment and a ball mill were performed in Ar ambient atmosphere. As a result of analyzing the end of Si, germanium, or aluminum-graphite composite powder it was obtained by this with a wide angle X-ray diffraction method, the peak which shows the diffraction from carbon, Si, etc. was observed. d002 of

carbon - 0.3358nm it was. Moreover, Lc was 45nm. The diffraction peak of carbide, such as Si, was not observed. moreover, an R value - 0.3 it was. As a result of observing the cross section in the above-mentioned end of composite powder, particles, such as Si, were laid underground in the graphite particle and mean particle diameter, such as Si, was about 2 micrometers. Moreover, such specific surface area in the end of composite powder was 63m² / g. The end of composite powder :P N-methyl pyrrolidone solution of PVDF and the end of composite powder were kneaded so that it might become the weight ratio of VDF=85:15, and it applied to Cu foil with a thickness of 20 micrometers. Pressurization molding of the electrode was carried out after 1-hour desiccation and with a roller press at 120 degrees C, and finally this was pierced in diameter of 20mm, and was made into the negative electrode.

[0117] The powder of LiCoO₂ with a mean particle diameter of 10 micrometers was used for positive active material. LiCoO₂ powder: Graphite :P It mixed so that it might become the weight ratio of VDF=90:6:4, and the slurry was formed. N-methyl pyrrolidone solution as well as [at this time] a negative electrode was used. This slurry was fully applied to aluminum foil with a thickness of 20 micrometers after kneading. Pressurization molding of the electrode was carried out after 1-hour desiccation and with a roller press at 120 degrees C, and finally this was pierced in diameter of 20mm, and was made into the positive electrode. here -- since the capacity of a negative electrode is large -- a negative electrode -- the positive electrode to a mixture -- the weight ratio of a mixture was set to 15.

[0118] The coin mold cell which shows the negative electrode and positive electrode which were produced at the above-mentioned process to drawing 1 was constituted, and the property was evaluated. the positive-electrode can 1 made from stainless steel -- positive-electrode charge collector 2a and a positive electrode -- a mixture -- the positive electrode 2 which consists of 2b was installed by spot welding. moreover, the negative-electrode can 3 made from stainless steel -- negative-electrode charge collector 4a and a negative electrode -- the negative electrode 4 which consists of mixture 4b was installed by spot welding. In both a positive electrode and a negative electrode, it is one mol [1.] LiPF₆ to the mixed solvent of 1:2 of ethylene carbonate (EC) and dimethyl carbonate (DMC). Infiltrated the dissolved electrolytic solution, the positive electrode and the negative electrode were made for the separator 5 made from polyethylene to counter by ****, and the positive-electrode can and the negative-electrode can were stuck by pressure with the insulating gasket 6.

[0119] This cell is charged by 1mA of charging currents, and charge termination electrical-potential-difference 4.2V, and it is 1mA of discharge currents, and discharge-final-voltage 2.7V. The charge-and-discharge cycle trial made to discharge was carried out. consequently, the initial discharge capacity of a cell -- 12.5mAh(s) it is -- the percentage of irreversible capacity was 24%. On the other hand, the discharge capacity maintenance factor of a 100 cycle eye to 1 cycle eye was 85%.

[0120] (Example 13) Drawing 8 is drawing showing the system configuration which carried the group battery module which produced 12 sets of group cells of the same specification as an example 9, and carried out the series connection of these group cells in the electric vehicle. The group battery module was installed in the car-body pars basilaris ossis occipitalis of an electric vehicle. When a driver operates a control device with a handle, the output from a group battery module is fluctuated and power is transmitted to a converter. The motor and the wheel were made to drive and it was made to run an electric vehicle using the power supplied from a converter. When an electric vehicle was driven by 1 charge at 80% of rated capacity, the deduction coefficient of capacity of the group cell after 100 transit was 2 - 5%. As a lithium secondary battery, examples 1-8 and the thing using a negative electrode given in 10-12 are incorporable into everything but this example similarly.

[0121] If a key switch is thrown in like the usual gasoline-powered vehicle and an accelerator is stepped on, he is trying to control the torque of a motor, or rotation according to an accelerator **** include angle. When an accelerator is returned, the regenerative brake equivalent to engine brake is operated, and the regenerative-brake force is made to increase further at the time of brake treading in. By the shift-lever signal, advance / go-astern change of a vehicle is performed, and the change gear ratio supposes that it is always fixed. The IGBT vector control inverter method using the induction motor as a control system was adopted, and in this example set to 336V from IGBT withstand voltage, supply voltage set the output to 45kW of maximum output, and maximum torque 176N-m from the power engine

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performance (acceleration and climb engine performance) as an automobile, and set rated output to 30kW from the full speed specification. It is made to perform fail-safe control other than advance / go-astern control of a vehicle, and regenerative control as a main control item.

[0122] Since a heat consistency becomes large by small and lightweight-ization of a motor, considering as efficient cooling structure becomes important. Since the temperature rise of a motor became high in general air cooling, it was made the water cooling type like the common engine.